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PROCESS OF ESTERIFYING ALDEHYDES.

No Drawing.

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Our invention relates to a process of esterifying aldehydes.

It is known that acetaldehyde in the presence of aluminum ethoxide may react with itself to give ethyl acetate, according to the equation $2\text{CH}_3\text{CHO} = \text{CH}_3\text{COO}.\text{CH}_2.\text{CH}_3$. We have now discovered that the usefulness of aluminum ethoxide in this catalysis may be greatly increased by the addition of a few percent of certain nitrates of acidic reaction. For example, zinc nitrate is such a promoter. Also, we may use nitrates of other metals whose hydroxyl compounds are weak bases. We have used such nitrates that are soluble in commercial ethyl acetate. Nickel nitrate is an example.

A specific example of one mode of practice of our invention follows. A solution of 9 g. aluminum ethoxide that has been made in the usual manner and then heated to 170°C . and 1 g. carefully dehydrated zinc nitrate in 100 g. dry commercial ethyl acetate, containing approximately 85 per cent of actual ethyl acetate and 15 per cent of ethyl alcohol, is allowed to flow slowly into a 1000 cc. flask, provided with stirrer and reflux condenser and set in an ice-water bath, while 400 cc. dry, freshly distilled acetaldehyde is also being admitted to the flask. Stirring is maintained and the temperature is not allowed to rise appreciably above 20°C . Within a few minutes after the last of the aldehyde and promoter-catalyst solutions have been introduced, the reaction subsides.

In one such experiment, we found less than 6 per cent of the original aldehyde not converted into ethyl acetate. In another experiment in which aluminum ethoxide alone was used as the catalyst without any zinc nitrate, fully 25 per cent of the aldehyde was left unconverted at the end of the test.

We have given this detailed example by way of illustration only. We may vary many of the conditions without departing from the invention. Thus we may use as the catalyst some other metal alkyl oxide, such as the ethoxide, isopropoxide, or butoxide of titanium or aluminum, and as the aldehyde propionic aldehyde, butyric aldehyde or a mixture of two different aldehydes, such as butyric aldehyde and acetaldehyde, in order to produce butyl acetate. Also, we may vary the proportions of the several ingredients, the method of introduction into the reacting vessel, the type of

equipment used, and the temperature of reaction.

The careful exclusion of water from all materials is necessary to prevent an incomplete esterification of the acetaldehyde. In drying the zinc nitrate, for example, we may dissolve crystallized zinc nitrate in anhydrous alcohol, evaporate to dryness, and then repeat the process once or twice, the final evaporation being completed in vacuo.

We claim:

1. In the process of converting an aldehyde to an ester in the presence of an alkyl oxide of a trivalent metal, the improvement which consists in using a promoter comprising the nitrate of a metal whose hydroxide is a weak base.

2. In the process of converting an aldehyde to an ester in the presence of an alkyl oxide of a trivalent metal, the improvement which consists in using a promoter comprising the nitrate of a metal whose hydroxide is a weak base, said nitrate being soluble in commercial, 85% ethyl acetate.

3. In the process of converting an aldehyde to an ester in the presence of an alkyl oxide of a trivalent metal, the improvement which consists in using a promoter comprising zinc nitrate.

4. In the process of converting acetaldehyde to ethyl acetate in the presence of an alkyl oxide of a trivalent metal, the improvement which consists in using a promoter comprising the nitrate of a metal whose hydroxide is a weak base.

5. In the process of converting acetaldehyde to ethyl acetate in the presence of an alkyl oxide of a trivalent metal, the improvement which consists in using a promoter comprising the nitrate of a metal whose hydroxide is a weak base, said nitrate being soluble in commercial, 85% ethyl acetate.

6. In the process of converting acetaldehyde to ethyl acetate in the presence of an alkyl oxide of a trivalent metal, the improvement which consists in using a promoter comprising zinc nitrate.

7. In the process of converting an aldehyde to an ester in the presence of aluminum ethoxide, the improvement which consists in using a promoter comprising the nitrate of a metal whose hydroxide is a weak base.

8. In the process of converting an aldehyde to an ester in the presence of aluminum

- ethoxide, the improvement which consists in using a promoter comprising the nitrate of a metal whose hydroxide is a weak base, said nitrate being soluble in commercial, 85% ethyl acetate.
9. In the process of converting an aldehyde to an ester in the presence of aluminum ethoxide, the improvement which consists in using a promoter comprising zinc nitrate.
10. The process of converting acetaldehyde to ethyl acetate which comprises the use of aluminum ethoxide and anhydrous zinc nitrate.
11. The process of esterifying acetaldehyde in the presence of a solution of approximately 9 parts by weight of aluminum ethoxide to 1 part of zinc nitrate.
12. The process of esterifying acetaldehyde in the presence of a solution of approximately 9 parts by weight of aluminum ethoxide to 1 part of zinc nitrate at a temperature not substantially above 20° C.
13. The process of converting acetaldehyde to ethyl acetate which comprises treatment with aluminum ethoxide that has been heated to approximately 170° C. and then dissolved, along with approximately one-ninth its weight of zinc nitrate, in ethyl acetate.
14. The process of converting an aldehyde to an ester which comprises the use of an ethyl acetate solution of aluminum ethoxide and zinc nitrate.
15. In the process of converting an aldehyde to an ester, in the presence of an alkyl oxide of a metal, the improvement which consists in using a promoter comprising zinc nitrate.
16. In the process of converting an aldehyde to an ester, in the presence of an alkyl oxide of a metal, the improvement which consists in using a promoter comprising a nitrate of a metal whose hydroxide is a weak base.
17. In the process of converting an aldehyde to an ester, in the presence of an alkyl oxide of a metal whose hydroxide is amphoteric, the improvement which consists in using a promoter comprising zinc nitrate.
18. In the process of converting an aldehyde to an ester, in the presence of an alkyl oxide of a metal whose hydroxide is amphoteric, the improvement which consists in using a promoter comprising a nitrate of a metal whose hydroxide is a weak base.

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